Concentrate of surfactant-based draw solutions in forward osmosis by ultrafiltration and nanofiltration

Hau Thi Nguyen, Nguyen Cong Nguyen, Shiao-Shing Chen and Shu-Ying Wu

ABSTRACT

The exploration of coupling surfactants with highly charged phosphate as novel draw solutions for forward osmosis (FO) to minimize salt leakage and enhance draw solute recovery at low energy is presented for the first time. In this work, anionic (sodium dodecyl sulfate (SDS)), cationic (cetyltrimethylammonium bromide) and non-ionic (polyethylene glycol tert-octylphenyl ether, TX-100) surfactants were used to couple with Na3PO4 for enlarging draw solution particle size that could improve the solute retention. Three kinds of nanofiltration (NF) membranes (HL, DL and TS80 with molecular weight cutoff (MWCO) of 100–500) and three kinds of ultrafiltration (UF) membranes (GE, GH and GK with MWCO of 1,000–3,000) were used to evaluate the draw solution recovery. The formed second layer, micelles, MWCO and charged valent were determined to be the dominant mechanisms for diluted draw solution recovery. The results show that coupling non-ionic surfactant with 0.02 M Na3PO4 can be regenerated with recoveries as high as 60% and 96% when using UF-GE and NF-TS80, respectively. The overall performance demonstrates that coupling surfactant with highly charged phosphate is promising as draw solutes for application to FO.

Key words | draw solution, forward osmosis, high charge, micelles, nanofiltration, ultrafiltration

INTRODUCTION

Forward osmosis (FO) is a process of water driven by the osmotic pressure difference across the semi-permeable membrane without the aid of external energy. Unlike other membrane process such as reverse osmosis (RO), FO can be operated at a low cost because of the absence of hydraulic pressure which makes it possible to be a promising technology. Recently, FO process has been applied in many places, such as power generation (McGinnis & Elimelech 2008; Jia et al. 2014), food processing (Petrotos et al. 1998, 1999), desalination (McCutcheon et al. 2005, 2006; Cath et al. 2006), osmotic membrane bioreactor (Achilli et al. 2009; Kim 2014) and medical and pharmaceutical applications (Yang et al. 2009). However, its application is still hindered due to the lack of effective diluted draw solution recovery. Draw solution regeneration using RO or thermal decomposition proved highly efficient but costly (McCutcheon et al. 2006; Achilli et al. 2010; Yen et al. 2010; Wang et al. 2011), meanwhile magnetic separators is troublesome with particle aggregation during recycling (Ling et al. 2010; Ge et al. 2011). Some draw solutions (CuSO4 and MgSO4) were recovered by using metathesis precipitation reaction (Alnaizy et al. 2013a, b), but adding chemicals will increase the cost of upgrading and secondary pollution to the environment.

Basically, the small molecular weight electrolytes and solutes used as a draw solution may not be economical because of the challenge of achieving low-energy recovery and the problem of salt leakage due to reverse diffusion of the draw solution across the membrane. Hence, in this study, three surfactants were proposed to couple with highly charged species of phosphate as the draw solutions to minimize the reverse flux of ions in FO and increase efficiency recovery of diluted draw solution using ultrafiltration (UF) or nanofiltration (NF).
systems at low energy. Surfactants present dual structural units: a hydrophilic group (polar group, the head) and a hydrophobic group (long hydrocarbon chain, the tail), which are classified according to the charged groups in the hydrophilic head including (i) anionic, (ii) cationic, and (iii) non-ionic. Micelles will be formed spontaneously in solution at concentrations above the critical micelle concentration (CMC), and micellar systems have been applied in food processing, chemicals and biotechnology (Schramm et al. 2005). In principle, at the CMC, surfactant solution aggregate to form micelles that could couple with highly charged phosphate to enlarge molecular size of draw solution, resulting in enhancing draw solute recovery with the aid of membrane process. The purpose of this research is to investigate the recovery of highly charged species of phosphate coupled with surfactants as the draw solutions for the following: (1) effect of different surfactants on water flux and reverse salt flux; (2) comparison of three kinds of NF membranes and three kinds of UF membranes; and (3) investigate the effects of coupling anionic (SDS), cationic (cetyltrimethylammonium bromide (CTAB)) and non-ionic (TX-100) surfactants for draw solution recovery.

MATERIALS AND METHODS

FO membrane

The flat-sheet cellulose triacetate (CTA) FO membranes used in this study were supplied by Hydration Technology Innovations (HTIs OsMem™ CTA Membrane 130806, Albany, OR, USA) with a size of 15 × 22 cm for each piece. The overall thickness of the membrane was approximately 50 μm, and the FO membrane was negatively charged at pH >4.5.

NF/UF membranes

In the last few years, the application of NF membranes have become popular, because of offering a variety of advantages such as low operating pressure, relatively low capital and maintenance cost and high rejection rates for multivalent salts (Liang et al. 2014). UF has attracted considerable attention because of its relatively low energy cost compared to RO and NF, and the decreasing cost of membranes (Gao et al. 2011). Table 1 shows the characteristics of the UF and NF membranes provided by Osmonics and TriSep for the draw solution recovery.

Chemicals

All the chemicals used in this study were of laboratory grade, and purchased from Sigma-Aldrich, UK and using deionized (DI) water as feed solution. The three surfactants used in this study, including their names, chemical formulae and properties, are listed in Table 2. The structural formulae of surfactants are shown in Figure 1.

Experiment setup

The experiment setup is shown in Figure 2 and the total effective FO membrane area was 41.40 cm². The feed and

| Table 1 | Characteristics of ultrafiltration and nanofiltration membranes |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Manufacturer   | UF-GE          | UF-GH          | UF-GK          | NF-HL          | NF-DL          | NF-TS80        |
| Material       | GE osmonics    | GE osmonics    | GE osmonics    | GE osmonics    | GE osmonics    | TriSep         |
| Composite      | Thin film      | Thin film      | Thin film      | Thin film      | Thin film      | Polyamide      |
| MWCO (Da)      | 1,000          | 2,000          | 3,000          | 150–300        | 150–300        | 150            |
| 25 C           | 1–11           | 1–11           | 1–11           | 3–9            | 2–10           | 2–11           |
| Range pH       |                |                |                |                |                |                |
| Rej-size       | 1K-PEG         | 2K-PEG         | 3K-PEG         | 98% – MgSO4    | 96% – MgSO4    | 99% – MgSO4    |
| Typical flux/psi| 31/400         | 34/150         | 29/75          | 66/100         | 53/100         | 34/110         |
| LMH@PSI        |                |                |                |                |                |                |
| Contact angle (°C) | 66.2       | 70.96          | 58.66          | 41 ± 2 (Verliefde 2008) | 54.4 (Cornelis et al. 2005) | 48 ± 2 (Verliefde 2008) |
draw solutions on both sides of the FO membrane were circulated by two peristaltic pumps (Master Flux L/S Drive, Model 7518-00) with a cross flow rate of 6.4 cm/s. Two water baths were used to maintain the temperature at 25 ± 0.5 °C during the experiment. Conductivity and pH sensors were installed in the containers to monitor any changes in the feed and draw solutions. A 1 L of feed solution tank was placed on a weighting scale (BW12KH, Shimadzu, Japan) which was connected to a computer data logging system to monitor weight and volume changes.

**Table 2** Summary of the surfactant properties

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Type</th>
<th>Molecular weight (g/mol)</th>
<th>Abbreviation</th>
<th>Critical micelle concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetyltrimethylammonium bromide</td>
<td>Cationic</td>
<td>364.45</td>
<td>CTAB</td>
<td>0.9</td>
</tr>
<tr>
<td>SDS</td>
<td>Anionic</td>
<td>288.38</td>
<td>SDS</td>
<td>8</td>
</tr>
<tr>
<td>Polyethyleneglycolter-octylphenyl ether</td>
<td>Non-ionic</td>
<td>647</td>
<td>TX-100</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**Figure 1** The structural formulae of SDS, CTAB and TX-100.

**Figure 2** Experimental setup of laboratory-scale FO/UF/NF hybrid system using highly charged phosphate coupled with surfactants as the draw solutions.
at regular time intervals. After FO, the dilute draw solution was recovered through the different UF and NF membranes for reuse by using a cross flow module (CF042 DelrinAcetal Cross Flow Cell, USA) under hydraulic pressures of 60 and 6.9 bar. The efficiency of the UF and NF is defined by the rejection factor, \( R \):

\[
R = \frac{1}{C_P/C_R}
\]

where \( C_P \) and \( C_R \) are the concentrations of the solutes in permeate and retentate, respectively.

**Analytical methods**

The concentration of phosphate was measured by colorimetrically according to Method 8178-Amino Acid Method using a UV–Vis spectrophotometer (Hach Model DR-4000) at a wavelength of 530 nm. The concentration of sodium was measured by direct potentiometric analyses using an ion meter (Metrohm Model 781). Surfactant concentrations were prepared using 0.45 \( \mu \)m filter paper, and then measured using an Aurora1010C TOC Analyzer (O.I. Analytical Corporation, USA). The osmolality of solutions was measured using an osmometer (Model 3320, Advanced Instruments, Inc., USA). The conductivity was determined by a conductivity meter (Sension156, Hach, China).

**RESULTS AND DISCUSSION**

**Effect of different surfactants on water flux and reverse salt flux**

Figure 3 shows the reverse salt fluxes (\( J_s \)) and water fluxes (\( J_w \)) for four draw solutions with various surfactants coupled with a Na\(_3\)PO\(_4\) concentration of 0.1 M. The concentrations of all surfactants were used at the CMC. It is observed that reverse flux reduced significantly when coupling SDS and TX-100 to Na\(_3\)PO\(_4\) draw solution. Compared with pure Na\(_3\)PO\(_4\) (\( J_s = 0.617 \text{ g/m}^2 \text{ h} \)), 0.1 M Na\(_3\)PO\(_4\) draw solution coupled with 10 mM SDS and 0.5 mM TX-100 exhibited less reverse salt flux (\( J_s = 0.184 \text{ g/m}^2 \text{ h} \) for 10 mM SDS and \( J_s = 0.0786 \text{ mM} \) MX-100). Strong hydrophobic interactions between tail groups of SDS and TX-100 with the membrane are believed to be the main mechanism for minimizing salt leakage. In contrast, the reverse salt flux of 1 mM CTAB coupled with 0.1 M Na\(_3\)PO\(_4\) draw solution was not reduced compared with SDS and TX-100. Moreover, the experiment results showed that water fluxes decreased slightly when using CTAB (\( J_w \) of 2.814/\text{m}^2 \text{ h} \)), SDS (\( J_w \) of 2.648 \text{ L/m}^2 \text{ h} \)) and TX-100 (\( J_w \) of 2.508 \text{ L/m}^2 \text{ h} \)) coupled with Na\(_3\)PO\(_4\) draw solution whereas their osmolality increased as shown in Table 3. This may be due to the increase in viscosity of draw solution when adding surfactants to Na\(_3\)PO\(_4\).

**Effect of different membranes on recovery of diluted draw solution**

Recovery of diluted draw solutions of 0.04 M Na\(_3\)PO\(_4\) coupled with 0.5 mM TX-100 in FO process was performed with the selected three UF and three NF membranes. Table 4 presents the experiments performed with the specific values of operating conditions. The results record that UF-GE achieved the highest recovery of 55.8\%, followed by UF-GH (47.17\%), and then UF-GK (45.56\%) from the conducted experiments, indicating that UF-GE had the smallest pore size (molecular
weight cutoff (MWCO) of 1000 Da), leading to retaining the diluted draw solution instead of passing through the membrane. By contrast, UF-GK generated the highest permeate flux of 24.7 L/m² h under hydraulic pressure of 5.5 bar, indicating that UF-GK was the loosest membrane and the production of permeate across the UF membrane was easier. Similarly, diluted draw solution was recovered using three NF membranes and the results demonstrated that NF-TS80 could achieve a retention of 97.05%, followed by NF-DL (91.40%), and NF-HL (90.24%).

**Concentrate of different diluted draw solutions**

The effect of different kinds of surfactants on recovering diluted draw solution is shown in Figure 4. The diluted draw solutions were prepared from 0.02 M Na₃PO₄ coupling with 0.5 mM TX-100, 1 mM CTAB, and 10 mM SDS. The results showed that the TX-100 achieved the highest retention efficiency of phosphate. Non-ionic surfactants are known to adsorb strongly to pores of UF membranes, therefore causing flux decline and a retention increase (Jijnssonl & Jijnsson 1991). In Figure 5, the retention decreased from 76 to 54% with increase in the phosphate concentrations from 0.02 to 0.1 M in the UF process. This behavior could be explained by the shielding phenomenon of the charged membranes (Baticle et al. 1997; Pauqam et al. 2004; Jermann et al. 2007). However, the retention of phosphate was high and stable (approximately 96.52%) when the concentrations of Na₃PO₄ were increased from 0.02 to 0.08 M using NF-TS80 as shown in Figure 6. An explanation for this phenomenon would be electrostatic repulsion and steric-hindrance effect. At pH 8, Na₃PO₄ was converted to divalent of HPO₄²⁻ and formed complex of NaHPO₄⁻ (simulated from Mineql+).

**Table 4** | Permeate flux (Jp) and retentions of different kinds of membranes using 0.04 M Na₃PO₄ coupled with 0.5 mM TX-100 as feed stream

<table>
<thead>
<tr>
<th>Membranes</th>
<th>TMP (bar)</th>
<th>Jp (L m⁻² h⁻¹)</th>
<th>TDS of permeate (g/L)</th>
<th>Rej (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF-GE</td>
<td>5.5</td>
<td>4.8</td>
<td>2.77</td>
<td>55.80</td>
</tr>
<tr>
<td>UF-GH</td>
<td>5.5</td>
<td>10.3</td>
<td>3.27</td>
<td>47.17</td>
</tr>
<tr>
<td>UF-GK</td>
<td>5.5</td>
<td>24.7</td>
<td>3.37</td>
<td>45.56</td>
</tr>
<tr>
<td>NF-HL</td>
<td>6.9</td>
<td>8.2</td>
<td>0.543</td>
<td>91.40</td>
</tr>
<tr>
<td>NF-DL</td>
<td>6.9</td>
<td>6.3</td>
<td>0.613</td>
<td>90.24</td>
</tr>
<tr>
<td>NF-TS80</td>
<td>6.9</td>
<td>3.7</td>
<td>0.185</td>
<td>97.05</td>
</tr>
</tbody>
</table>

**Figure 5** | Variations of PO₄-P retention and permeate flux at various Na₃PO₄ concentrations coupled with 0.5 mM TX-100 using UF-GE membrane at a pressure of 5.5 bars.

**Figure 6** | Variations of PO₄-P retention and permeate flux at various Na₃PO₄ concentrations coupled with 0.5 mM TX-100 using NF-TS80 membrane at a pressure of 6.9 bars.
based on chemical equilibrium model from the thermodynamic database) according to Figure 7. Since NF-TS80 membrane was negatively charged, negative charged membrane repulsed the negative charged HPO$_4^{2-}$ and NaHPO$_4^{-}$ leading to increased efficiency of solute rejection. In addition, the formed second layer of TX-100 on membrane surface enhanced solute retention (Ku et al. 2005).

CONCLUSIONS

This study presents the retention comparison of coupling CTAB, TX-100 and SDS with Na$_3$PO$_4$ by FO and UF/NF membranes in a cross flow module, and the results showed that the rejection order is TX-100 > SDS > CTAB. It was found that the formed second layer, micelles, MWCO, charged valent and hydrophobicity interactions were the dominant mechanism for the retention of solutes. For FO tests, the reverse salt fluxes of 0.1 M Na$_3$PO$_4$ coupled with 10 mM SDS and 0.5 mM TX-100 were reduced three and eight times more than pure Na$_3$PO$_4$, resulting in a significant decrease in the cost for replenishing lost draw solute. Moreover, the result of using different UF and NF membranes demonstrated that the UF-GE and NF-TS80 achieved the highest solute retention.

REFERENCES


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